Fused silica capillary interferometer with a layer-by-layer functional coating for the analysis of chemicals content in aqueous solutions

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ABSTRACT

A simple fused silica capillary interferometric (FSCI) sensor has been proposed and investigated for the detection and analysis of multiple chemical compounds content in aqueous solutions. The sensor was fabricated by splicing a commercially available fused silica capillary (FSC) with two single mode fibers to create a 0.7 cm long air cavity. The fiber surface was functionalized with two different polymers: poly (allylamine hydrochloride) (PAH) and sol-gel silica in sequence using a layer-by-layer deposition method. The operating principle of the sensor relies on light interference in the fused silica capillary cavity due to adhesion of the different chemical compounds on the functional coating surface. Studies of the sensors response to the presence of five different compounds in water solutions at different concentrations have been carried out and the results have been analyzed using the principal component analysis (PCA). This work is a preliminary investigation towards the development of a novel method for assessment of content and quality of alcoholic beverages in real time using functionalized FSCIs.

Keywords: Fiber optic sensor, interferometer, Principal component analysis

1. INTRODUCTION

Increasing public concern with food quality and safety is driving the need for simple and cost-effective techniques for the authentication of raw materials and finished foods. One example is assessment of the quality of alcoholic beverages, their origin, and their content to ensure adequate standards of production, uniformity within a brand, and to avoid falsification. Concentration of ethanol is an important parameter for all alcoholic beverages. The presence of other alcohols such as methanol, propanol and butanol even in low concentrations, either as a result of falsification or due to improper preparation processes, can cause adverse effects on human health. Moreover, while ethanol and water are the main chemicals present in all alcoholic beverages, numerous volatile and non-volatile flavor compounds are also present, and their analysis is important to ensure proper quality standards. Existing analytical techniques such as gas/liquid chromatography or mass spectrometry provide the most accurate assessment of the beverage content but while being the most specific and sensitive, they are complex, time-consuming, and both resource and labor intensive.[1,2] Optical fiber sensors (OFSs) can offer many advantages due to their high sensitivity and rapid response. For example, evanescent OFSs can detect minute changes in their surrounding refractive index (RI) and became very popular in many biological/ or chemical sensing applications. Such sensors operate through functionalizing their surface in order to convert the changes in the bio/chemical analyte into an RI variation.[3] Ning et al. reported a PDMS-coated Fabry-Perot fiber sensor for the detection of ethanol and other volatile compound concentrations in a gas mixture.[4] Additionally a long period grating (LPG) modified with a mesoporous film of 5 to 15 layers of PAH/SiO2 has been reported for the assessment of beverages quality.[5]

In this work we report on an investigation of a novel fused silica capillary interferometric fiber optic probe functionalized using layer-by-layer deposition of PAH/silica gel for characterization of several different aqueous solutions of chemical compounds significant in quality assessment of alcoholic beverages. The fiber probe was fabricated from a 0.7 cm long fused silica capillary, spliced with standard single mode fibers (SMF-28) at both ends to form an interferometric structure with interference dips in its transmission spectrum. Aqueous solutions of five different compounds: ethanol, methanol, citric acid, sugar and isopropyl with concentrations ranging from 5% to 25% w/w have been characterized by measurement of the shift of the selected transmission dip for the sensor probe immersed in each of the solutions. A principal component analysis (PCA) has been employed in order to determine the suitability of the proposed sensor to discriminate different types of chemical compounds.

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2. EXPERIMENTAL INVESTIGATION

2.1 Materials

PAH(Mw:50000), tetra ethyl orthosilicate (TEOS), potassium hydroxide (KOH), ethyl alcohol (99.5%), citric acid, glucose, isopropyl (99.8%) alcohol and hydrochloric acid (HCL, 37%) from Sigma-Aldrich were used as received without further purification. Deionized water (DI) (18.3 ΩM cm) was obtained by reverse osmosis followed by ion exchange and filtration (Millipore, Direct-QTM). Porous silica gel was prepared in the laboratory by sol-gel polymerization of tetra orthosilicate under hydraulic conditions using either acids or base catalysis. The molar ratio of TEOS, ethyl alcohol and DI water was 1:4:16 mixed in a 250-mL measuring flask and kept at continuous stirring conditions for 1.5 hour. 3-4 drops of hydrochloric acid (HCL) were used as catalyst. The solution was kept for two days at room temperature.[6]

2.2 Fiber optic structure fabrication and coating

A small portion of the polymer jacket was removed from a fused capillary (cap/010/150/24T, Fiberguide) with an outer diameter of 125 μm and an inner diameter 10 μm using heat source. Then a short length of the polymer jacket stripped-capillary was spliced at both ends with two standard single mode fibers (SMF-28). Both the single mode fibers and the capillary fiber have core diameters of 10μm. Fig.1(a) illustrates a schematic ray diagram of the capillary tube interferometric sensor. The microscopic image of the cross-sectional view of the tip of the cleaved capillary fiber is shown in Fig. 1(b). Following the splicing process, a mesoporous film composed of silica nano- spheres was deposited on the surface of the fiber structure using a layer-by-layer deposition method similar to the technique proposed by Korposh et al. in.[5] In our experiments in order to functionalize the surface of the FSCI, the following procedure was followed as illustrated schematically in Fig.1 (c). The FSCI structure was first rinsed with DI water and then dipped in a 2 % w/w alcoholic KOH (ethanol/water=3:2, v/v) solution for 30 minutes to enrich the surface of the fiber with negatively charged OH groups. The negatively charged surface of the FSCI structure was then immersed into a positively charged 16% w/w PAH solution for 5 minutes and then in a silica gel for 20 minutes to ensure chemical bonding with the negatively charged silica microspheres present in the silica gel. The structure was then rinsed with DI water to flush any residual unbound silica microspheres from its surface. Then the sample was dried for 24 hours at room temperature.

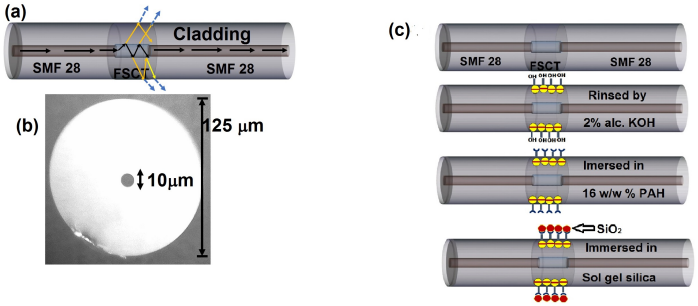

Figure 1. (a) Schematic diagram of the FSCI structure; (b) Microscopic image of the cross section of fused silica capillary (FSC); (c) Schematic illustration of the layer-by-layer deposition of PAH/silica gel

3. RESULTS AND DISCUSSION

The characterization setup for the FSCI fiber sensor consisted of a broadband light source (Thorlabs S5FC1005S), polarization controller and optical spectrum analyzer (OSA, Advantest Q8384). The coated FSCI fiber sensor was mounted on a PDMS coated glass slide. Light from the broadband source operating in the wavelength range 1530-1570 nm was launched into the input single mode fiber through a polarizer and the corresponding transmission spectrum was observed at the other end of the fiber probe using an OSA. The wavelength resolution of the OSA was 0.1 nm. When the light is launched in the silica capillary section, it propagates within the hollow core and glass cladding of the capillary experiencing reflections from both air-cladding and glass-(outer) air interfaces. Multiple reflections within the air core and silica cladding interfere resulting in the periodic dips in the output transmission spectrum. The loss within the capillary cavity increases with the increase in its length. In our case the cavity length was around 0.7 cm and we observed transmission dips at 1569.61 nm and 1597.02 nm with the extinction ratio of ∼10 dB as shown in Fig 2(a).

As an initial step to characterize the sensor, we studied the sensitivity of an uncoated FSCI structure to the surrounding RI. For this study a series of aqueous solutions of ethanol with concentrations of 5%, 8.8%, 14.3%,

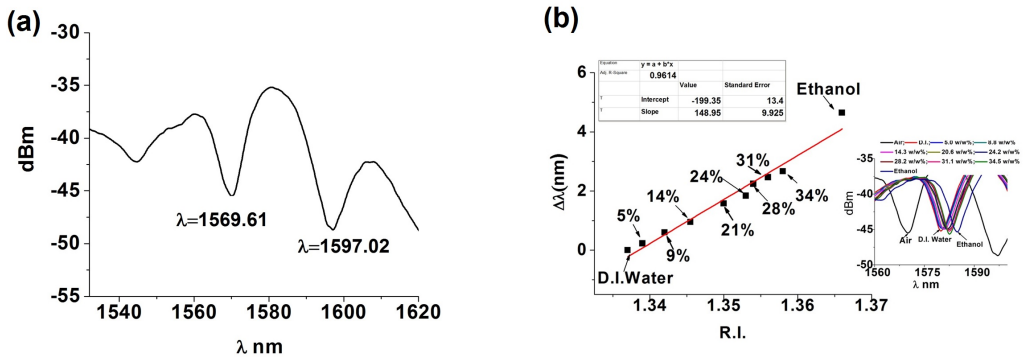

Figure 2. (a) Typical measured transmission spectrum of an FSCI structure with a 0.7 cm length of FSC; (b) Spectral shift of the FSCI transmission spectrum versus refractive index realized with different concentrations of ethyl alcohol in aqueous solution.

20.6%, 24.2%, 31.1%, 38% and 100% were prepared and tested. The RIs of these solutions were measured with the help of a portable Abbey refractometer. It was found that for a range of ethanol concentrations from 0% to 100% the RI of the solutions ranged from 1.337 to 1.366 respectively. The FSCI probe was then immersed in each of the prepared solutions and the spectral shift of the original transmission dip at 1569.61 nm was recorded. As it can be seen from Fig.2 (b), as the ethanol concentration in the solution increases from 0% to 100%, the selected transmission dip experiences a red shift of 4.65 nm, resulting in RI sensitivity of 148 nm/RIU. The inset graph in Fig. 2(b) illustrates the red shift of the transmission spectra with the increase of ethanol concentration. Then a functional PAH/silica gel coating was applied to the FSCI surface as described in the previous section. As illustrated in Fig. 3(a), coating of the FSCI structure with the PAH/silica gel layer led to the spectral shift of the original transmission dip at 1569.61 nm towards longer wavelengths by 7.2 nm, after which the transmission spectrum of the fiber structure remained stable during the following 24 hours. The RI sensitivity of the sensor was then characterized in the same set of solutions for the coated sensor and the results of the tests are combined in Fig. 3(b). As can be seen from the figure, sensitivity to the surrounding RI is increased by 20% in comparison with the uncoated sensor.

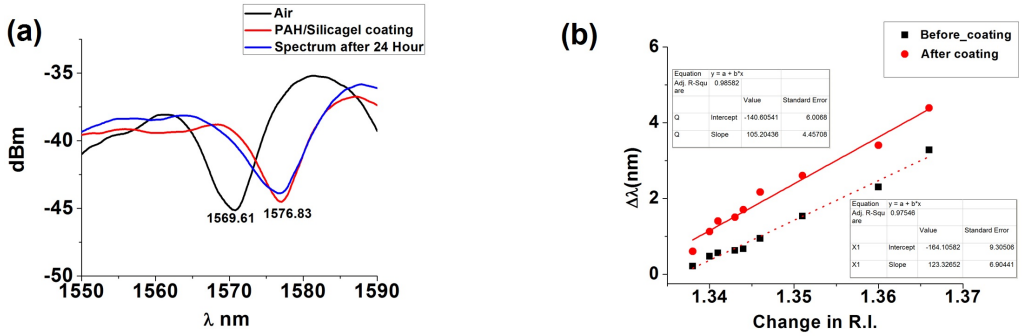

Figure 3. (a) Transmission spectra before and after coating with PAH/silica gel; (b) Dip spectral shift versus RI.

Subsequently we measured the coated FSCI structures response in aqueous solutions of five different chemical compounds, namely, in ethanol, methanol, citric acid, sugar and isopropyl with a range of known concentrations of 5%, 10%, 15%, 20% and 25% w/w. These five chemical compounds were chosen for the experiments since they play a significant role in the manufacture of alcoholic beverages. Fig.4 (a) shows the scatter plot of the dip spectral shifts in the above solutions versus their concentrations. As can be seen from the figure, the dip shifts in response to the different chemicals are almost linear with different slopes with respect to the concentration. Applying principal component analysis (PCA) to the data presented in Fig. 4(a) should allow the determination of unknown concentrations of the above chemicals in a mixture. PCA is a statistical method realizing conversion of a set of observations of possibly correlated variables into a set of linearly uncorrelated variables called principal components based on orthogonal transformation.[7] PCA analysis reduces the number of variables by merging correlated variables from the data set that are responsible for maximum variance in the output. Fig. 4 (b)

illustrates the results of application of the PCA analysis to the data shown in Fig. 4(a). As can be seen from Fig. 4 (b), the first principal component (PC1) is responsible for 86% variance, and the first two components (PC1 and PC2) together explain 95.1% variance, which is sufficient for a qualitative analysis of the data. Fig. 4(b) is a so called loading plot, visually illustrating the results for the first two principal components. The larger the absolute value of the component for a certain chemical, the more important the corresponding variable is in calculating the component. As can be seen from the graph, citric acid and ethanol have similar and relatively small principal values near the intercept of PC1 and PC2 whereas isopropyl and sugar have large positive (and negative) associations with both PC1 and PC2. Methanol has a large negative principal value along the PC1 which makes it clearly distinct from the other chemicals. The plot indicates that the proposed sensor can be used for the detection of important compounds in beverages. For example, PC1 values can be used to detect the presence of methanol, an alcohol closely related to ethanol, but much more toxic to humans. The potential for its presence in drinks made from home-distilled spirits is a serious health risk. The PC2 values can be used for classification of beverages by their sweetness.

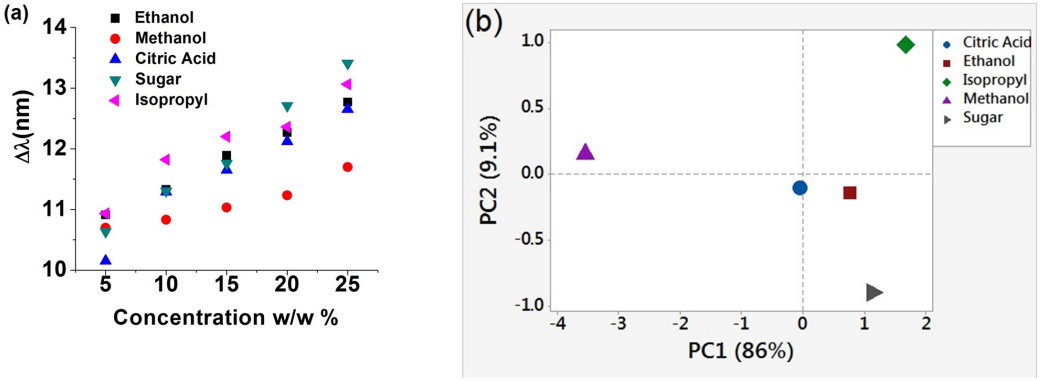

Figure 4. (a) Transmission spectra before and after coating with PAH/silica gel; (b) Dip spectral shift versus RI.

4. CONCLUSION

A simple FSCI structure functionalized with a PAH/silica gel has been proposed and investigated for applications in the analysis of various chemical compounds content in aqueous solutions. This study is a preliminary investigation to underpin the development of a novel method for assessment of the quality of alcoholic beverages in real time using functionalized FSCIs.

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